Lab-Scale Assessment of a Post-Combustion Carbon Dioxide Capture Process Enabled by a Combination of Enzymes and Ultrasonics

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DOOSAN

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UK UNIVERSITY OF KENTUCKY
Center for Applied Energy Research

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Notices

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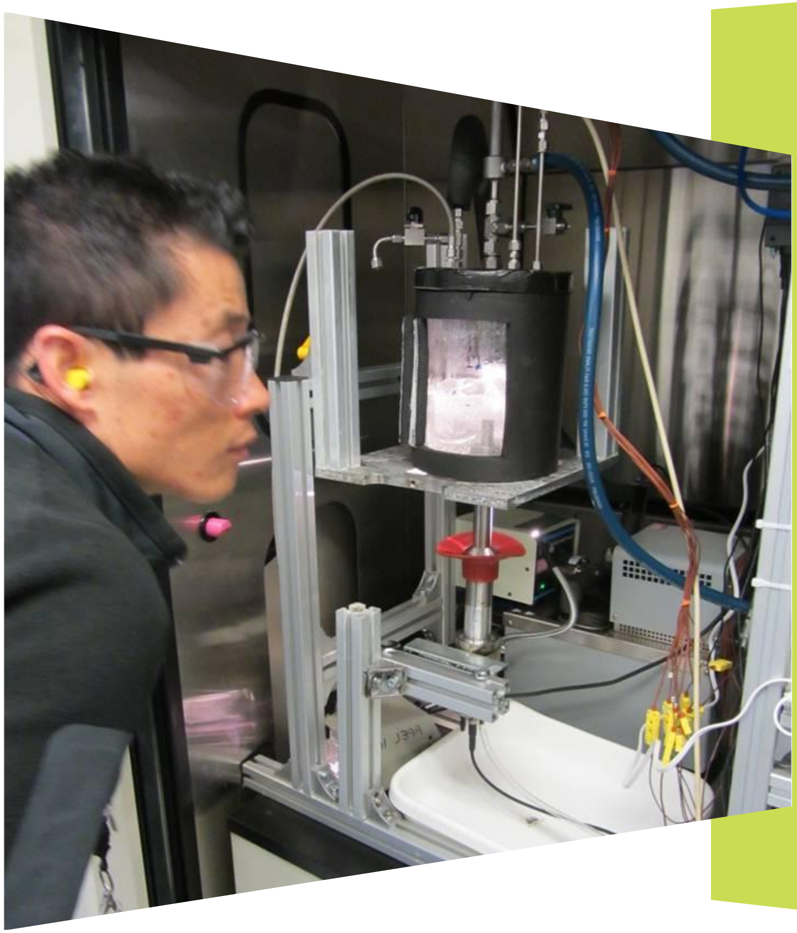
Agenda



- Project Overview
  - Project Partners and Objective
  - Process Concept
- Laboratory Validations
  - Ultrasonic Unit Batch Testing
  - Enzyme-Solvent Compatibility
  - Absorption Kinetics
- Next Steps
  - Prefeasibility Assessment
  - Plans for Bench-scale Evaluation

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Project Overview

- Project Participants

Pacific Northwest National Laboratory — Ultrasonics & Aspen®

Doosan — Full Process Analysis

Novozymes — Enzymes & Solvents

UK University of Kentucky Center for Applied Energy Research — Kinetics & Bench-scale Tests

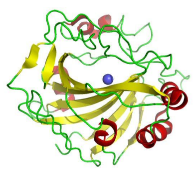
- DOE Project Manager: Andrew Jones
- Project Number: DE-FE0007741
- Total Project Budget: $2,088,643
- Project Duration: Oct. 1,2011 – Dec. 31, 2014

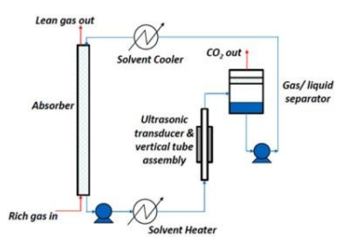
DOE Program Objectives
Develop solvent-based, post-combustion technology that
- Can achieve ≥ 90% CO_2 removal from coal-fired power plants
- Demonstrates progress toward the DOE target of <35% increase in LCOE.

Project Objective

Complete a *bench-scale study* and corresponding full technology assessment to validate the potential in meeting the DOE Program Objectives of a *solvent-based post-combustion carbon dioxide capture* system that <u>integrates</u>

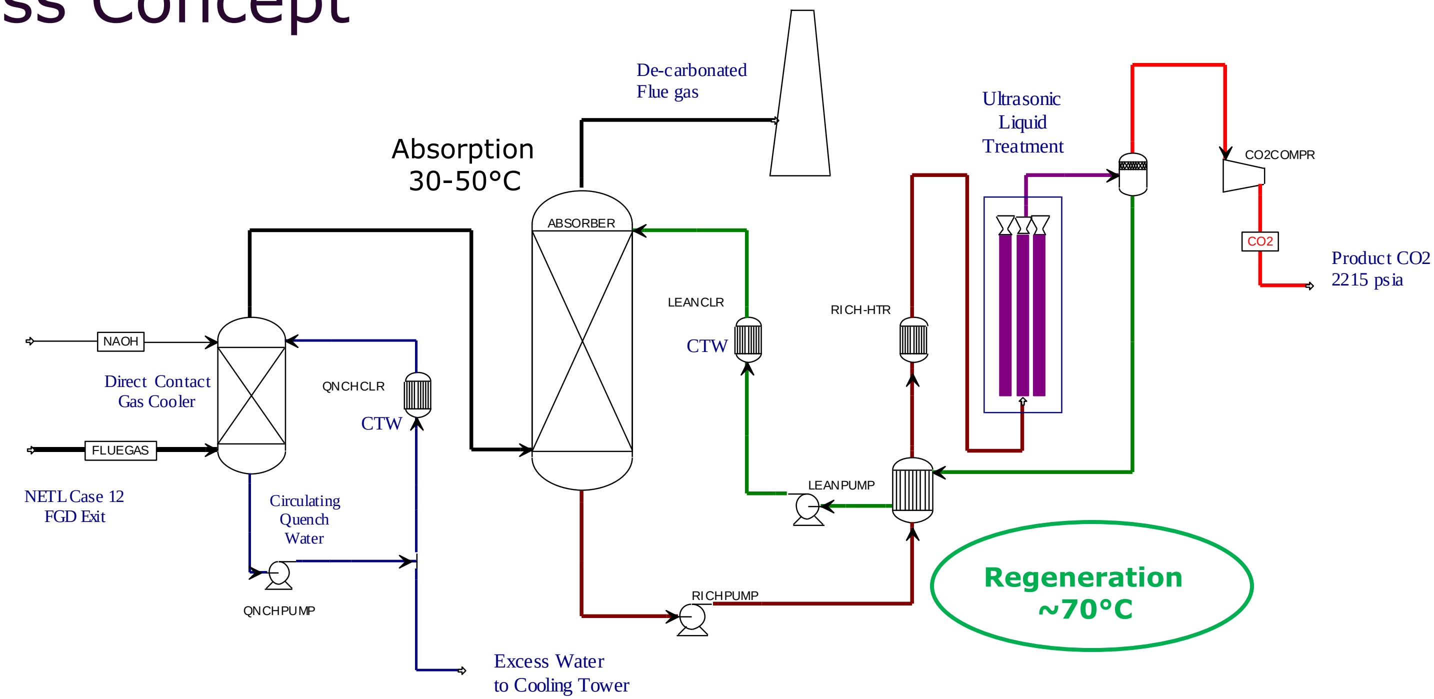
$CO_2 + H_2O + K_2CO_3 \leftrightarrow 2KHCO_3$





- a **low-enthalpy**, aqueous potassium carbonate-based solvent
- with an **absorption**-enhancing carbonic anhydrase enzyme catalyst
- and a flow through ultrasonic-enhanced **regenerator**
- in a **re-circulating** absorption-desorption process configuration

Process Concept



- *Advantages*

➢ Low enthalpy, benign solvent (catalyzed aq. 20% K_2CO_3)

  - K_2CO_3 ΔH_{rxn} 27 kJ/mol CO_2
  - MEA ΔH_{rxn} 83 kJ/mol CO_2

➢ Potential for ~50% regeneration energy vs. MEA

- *Challenges*

➢ Demonstrate atmospheric regeneration at 70°C enabled by ultrasonics

➢ Demonstrate overall techno-economic feasibility

  - energy demand
  - enzyme requirement

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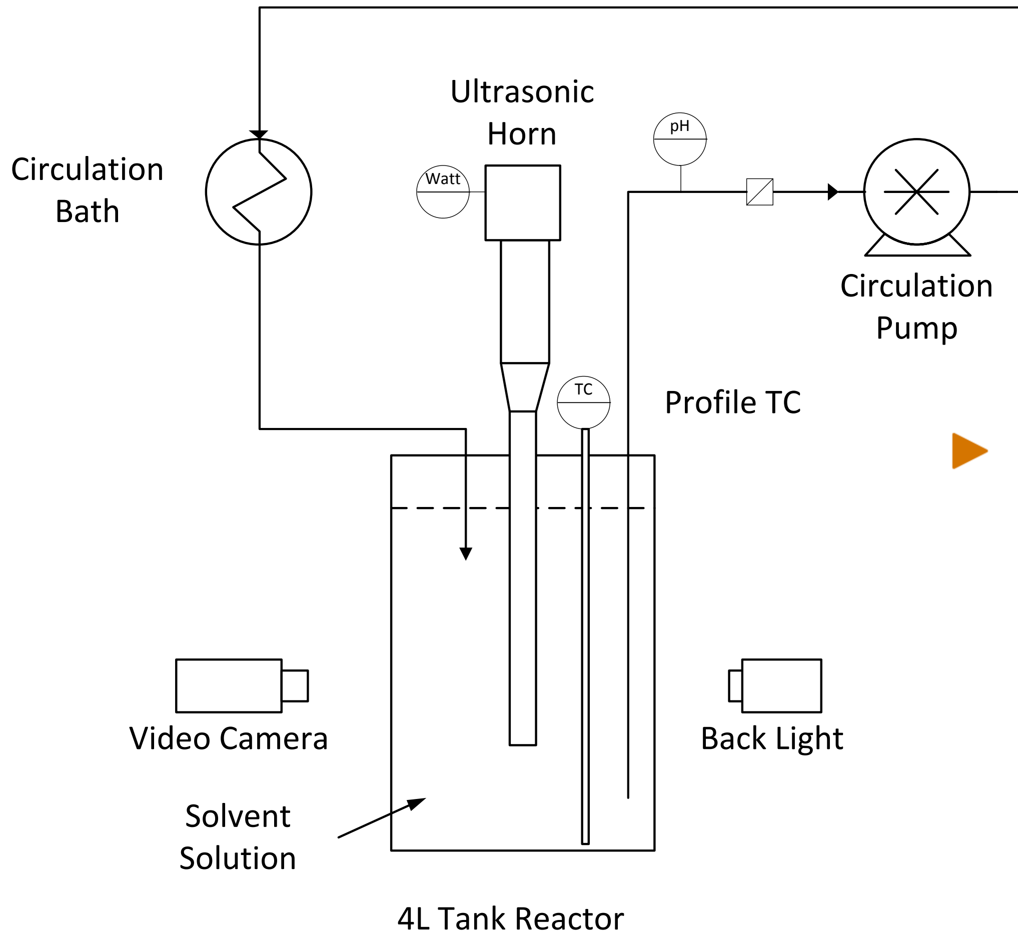
Laboratory Validations – Part 1

- Ultrasonic Unit Batch Testing
  - Demonstrated CO_2 release via ultrasonic energy addition
    - 1/3rd of target defined by ASPEN®-predicted vacuum
  - Established preliminary settings for ultrasonic power, frequency, exposure times, and need for continuous bubble removal

Ultrasonics Regeneration Mechanism

- Create a population of seed bubbles above a critical radius via ultrasonic cavitation in the liquid
- Bubbles expand and shrink in an ultrasonic field
  - Expanding bubbles = lower pressure/ higher surface area
  - Shrinking bubbles = higher pressure/ lower surface area
- Rectified diffusion results when expanding bubbles allow for a biased transfer of dissolved gas into the bubble from solution
  - Frequency optimization likely required due to its impact on the threshold pressure, and bubble growth
- Remove bubbles grown via rectified diffusion before they can dissolve back into the liquid

PNNL Lab Ultrasonic Desorption System Schematic



- System allows for introducing ultrasonic power while maintaining temperature to within 2°C.

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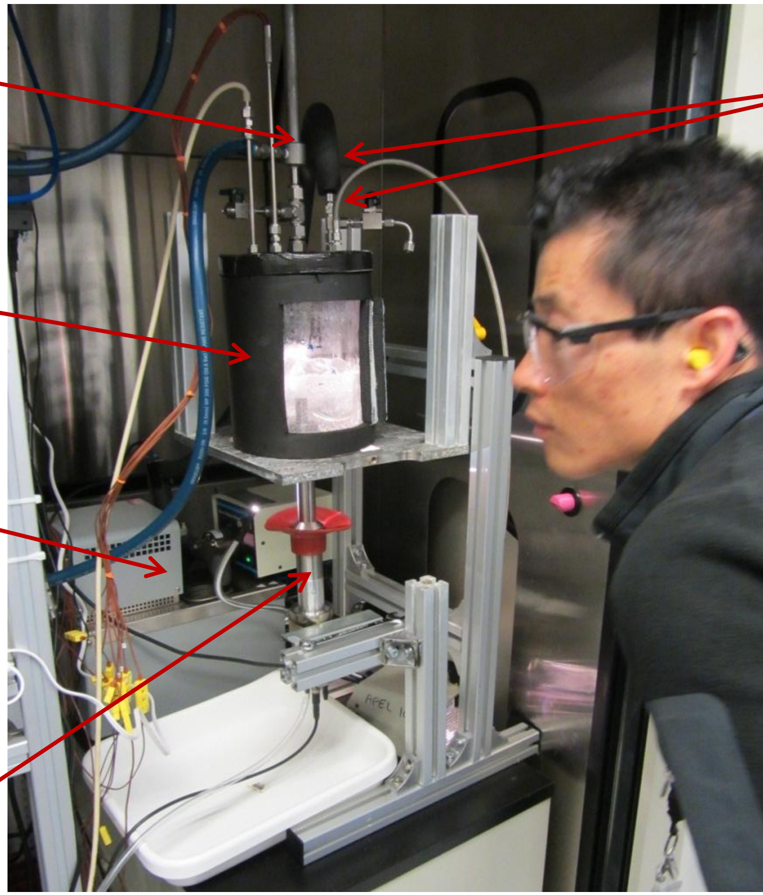
PNNL's Batch Lab Ultrasonic Desorption System

Gas Exit w/ Condenser

Vessel

Temperature Controlled Bath

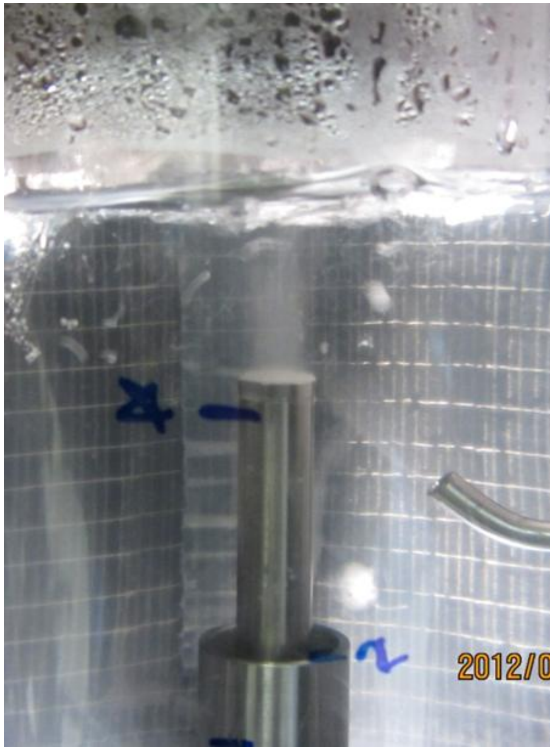
Ultrasonic Horn (inverted horn configuration)



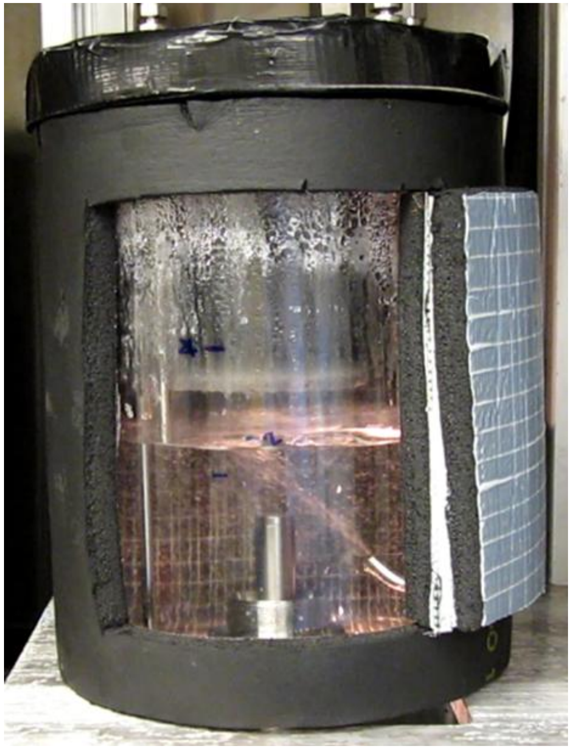
Solvent Recirculation Lines

- Bubbles expand and shrink in an ultrasonic field
- Rectified diffusion results when expanding bubbles allow for a biased transfer of dissolved gas into the bubble from solution
- Remove bubbles before they can dissolve back into the liquid

Photographs of Ultrasonic Desorption



Pure Water at 70°C – With Sonication

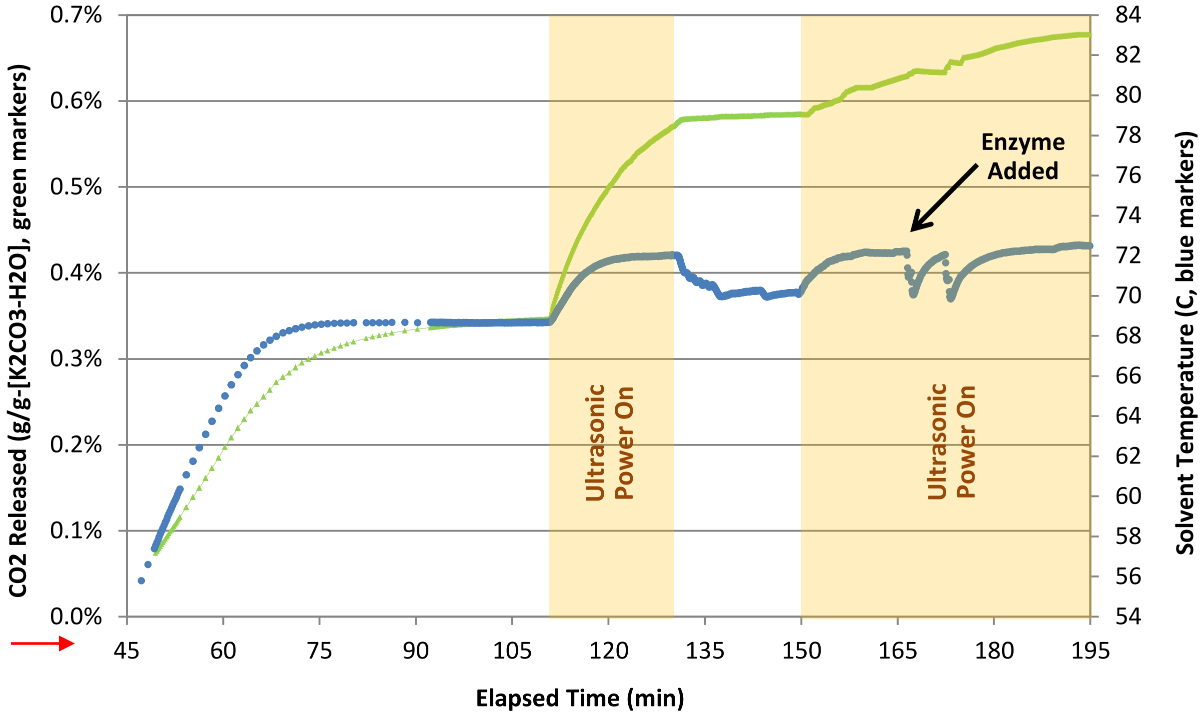


Loaded Solvent at 70°C – No Sonication

Loaded Solvent at 70°C – With Sonication

Significant agitation/ bubbling observed when ultrasonic power added to CO_2 loaded 20% K_2CO_3 solution at 70°C

Batch Test Results for Ultrasonic Regeneration



Pre-swept the gas-tight headspace with humidified CO_2

- Testing with 20 wt% K_2CO_3 solvent loaded to 4.6 wt% CO_2
- ASPEN (equilibrium) projections of CO_2 release at 6 psia = 0.96%
- Total CO_2 release observed = 0.67% (0.25% from ultrasonic effect)
  - Likely impacted by re-dissolution of CO_2
- Slow CO_2 release rates observed
  - Further evaluation needed

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Energy Projections for Ultrasonic Regeneration

- Commercial water sterilization = 0.24 to 0.79 kJe/ kg of water
  - Based on developed applications for ship ballast treatment [1]

- Initial batch testing for CO_2 regeneration = 4.9 kJe/ kg of solvent
  - Laboratory horn used. Poor CO_2 removal (significant re-dissolution)
  - Demonstrated value = 10.3 kJe /mol of CO_2, 0.021 kg of CO_2 removal per kg of recirculated solvent recirculation assumed.

- Full-scale CO_2 regeneration system estimate = 1.5 kJe/ kg of solvent
  - Based on (conservative) tube sonication configuration
  - Equates to just over 11 MWe of parasitic power for the ultrasonic system in the 500 MWe reference system

[1] "Ballast water treatment technology, Current status," February 2010 (http://www.lr.org/Images/BWT0210_tcm155-175072.pdf)

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Laboratory Validations – Part 2

- Ultrasonic Unit Batch Testing
  - Demonstrated CO_2 release via ultrasonic energy addition
    - 1/3rd of target defined by ASPEN®-predicted vacuum
  - Established preliminary settings for ultrasonic power, frequency, exposure times, and need for continuous bubble removal
- Enzyme-Solvent Compatibility
  - Lab results show robustness to simulated process pH, ultrasonics, and absorber temp. with (manageable) losses at increased temp.

Producing Enzymes for Industrial Applications

1. Improving the production host
Improving the microorganisms' ability to produce more enzymes per m^3 fermentation tank through genetic engineering

2. Optimizing the industrial production Traditional production optimization
- Process optimization
- Equipment optimization
- Input optimization

3. Improving the enzyme produced
Improving the efficacy of the enzymes through protein engineering to meet application conditions and process economy requirements

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Enzyme-Catalyzed CO_2 Sorption Mechansim

Carbonic anhydrase catalyzes (increases kinetic rates) the hydration of CO_2 and dehydration of bicarbonate resulting in enhanced absorption and desorption of CO_2 into and out of a CO_2 absorber solvent.

Low H_2O solubility

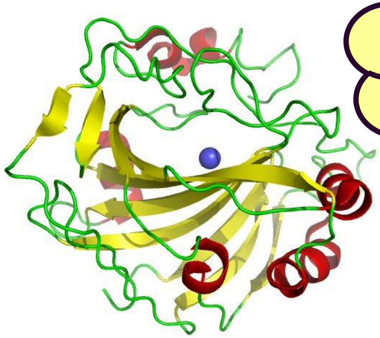
ydration / Absorptio

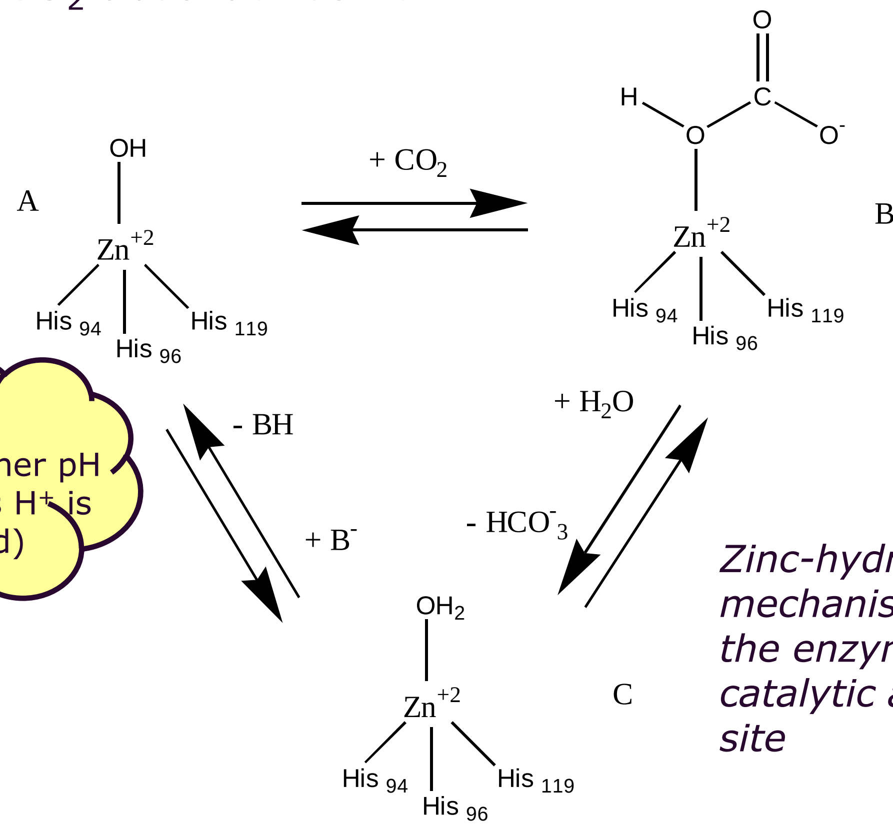
High H_2O solubility

$$H_2O + CO_2 \underset{}{\overset{CA}{\rightleftharpoons}} HCO_3^- + H^+$$

Dehydration/ Desorption

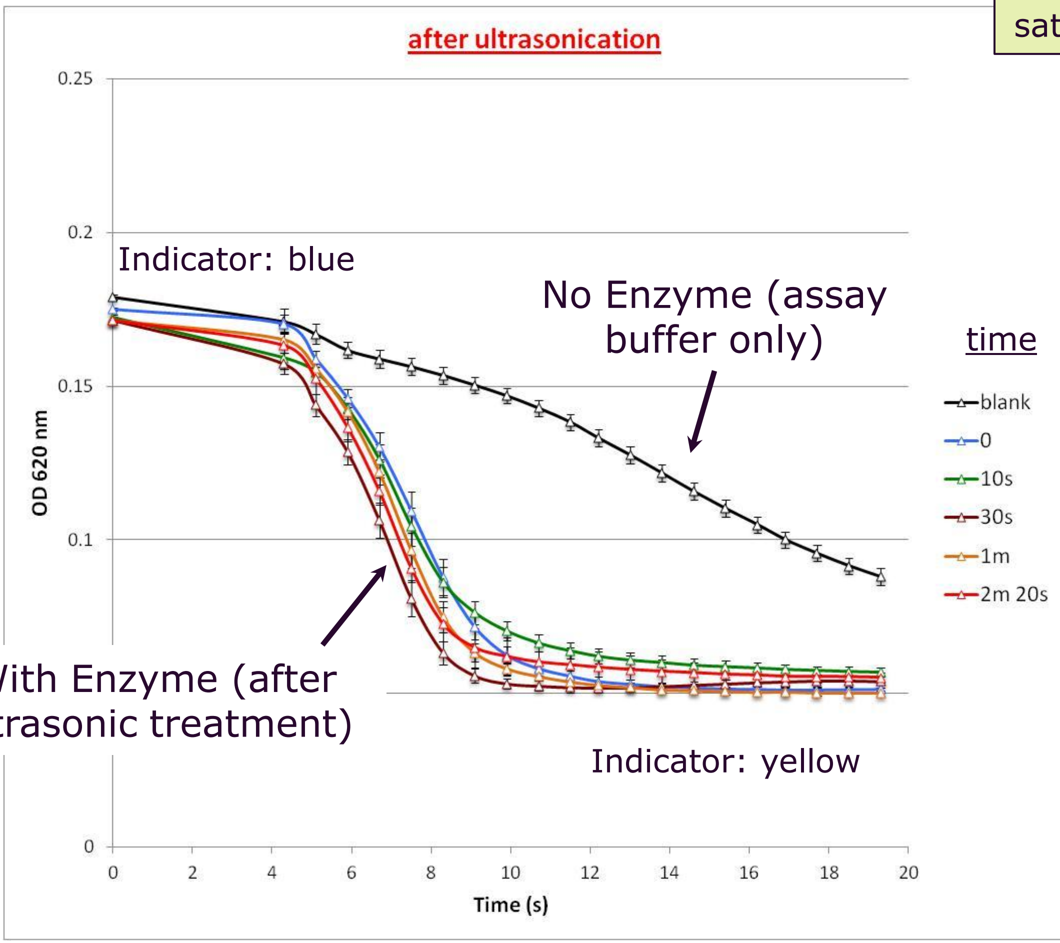
Reaction goes forward at higher pH (pH drops as H^+ is produced)



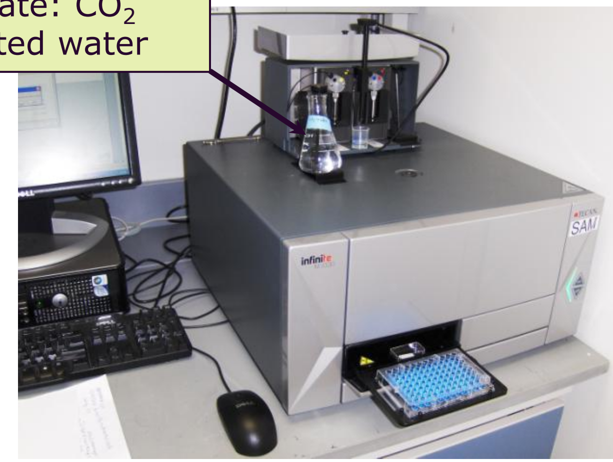


Zinc-hydroxide mechanism at the enzyme's catalytic active site novozymes Rethink Tomorrow

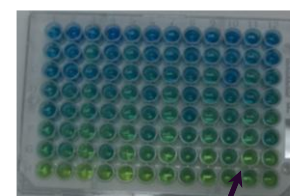
Enzyme Compatibility with Ultrasonic Treatment



Substrate: CO_2 saturated water



Indicator color changes due to pH decrease when CO_2 is hydrated to bicarbonate



$$CO_2 + H_2O \overset{CA}{\leftrightarrow} H^+ + HCO_3^-$$

- **Enzyme tolerates initial ultrasonic tests** with no apparent loss of activity

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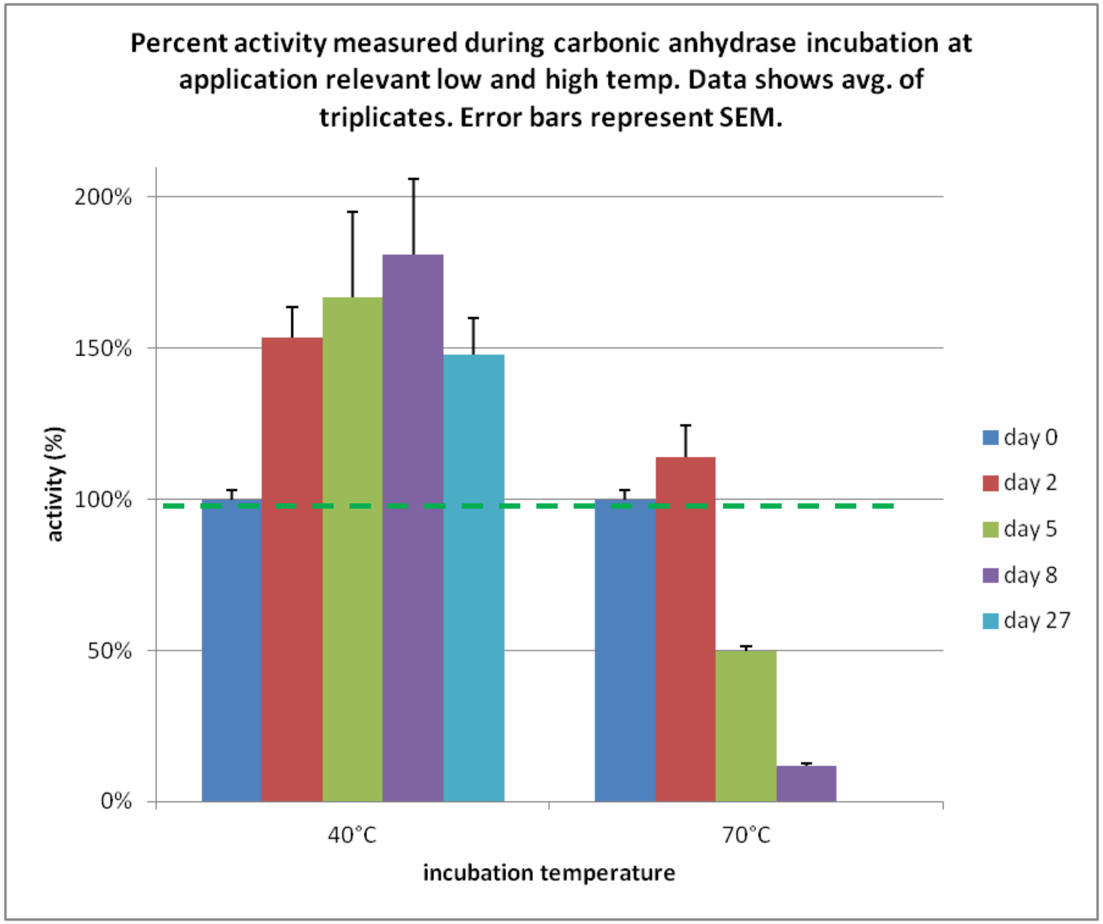
Enzyme-solvent Compatibility



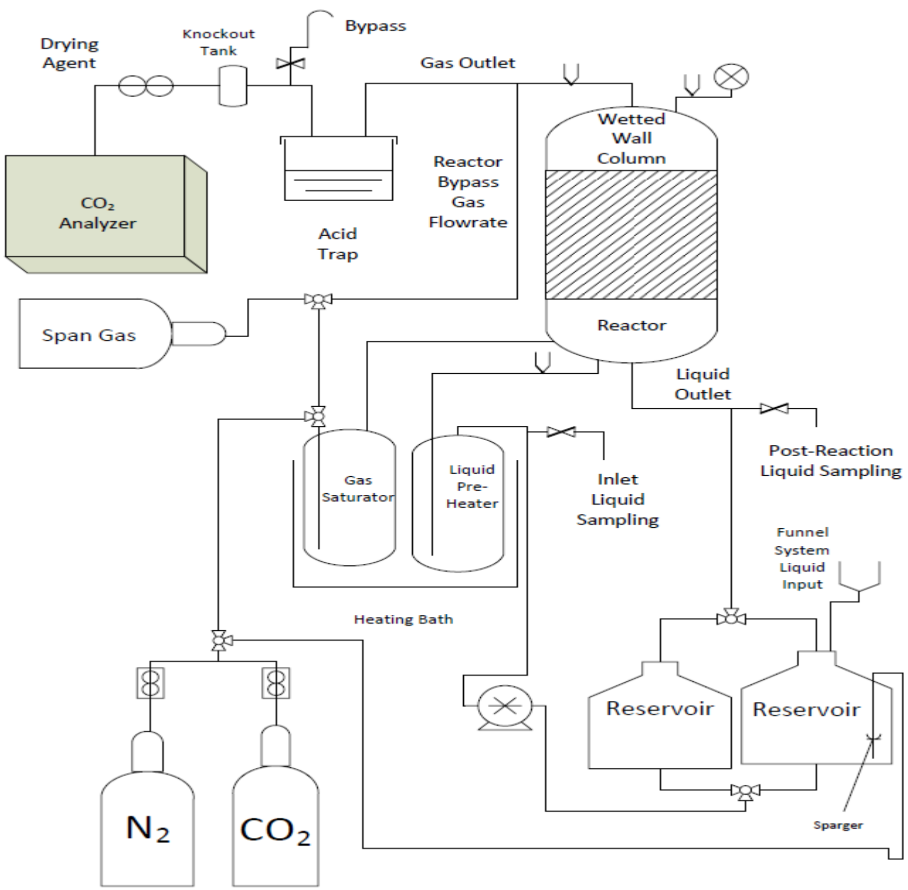
- Demonstrates high robustness in working solvent at 40°C
- Demonstrates limited (but nevertheless useful) robustness at 70°C
- Data used for initial estimation of solvent replenishment rate in prefeasibility

Solvent: aq. 22% $K_2CO_3/KHCO_3$ with 3 g/L enzyme and adjusted to lean pH

Laboratory Validations – Part 3

- Ultrasonic Unit Batch Testing
  - Demonstrated CO_2 release via ultrasonic energy addition
    - 1/3rd of target defined by ASPEN®-predicted vacuum
  - Established preliminary settings for ultrasonic power, frequency, exposure times, and need for continuous bubble removal
- Enzyme-Solvent Compatibility
  - Lab results show robustness to simulated process pH, ultrasonics, and absorber temp. with (manageable) losses at increased temp.
- Absorption Kinetics
  - Temperature had minimal impact on mass transfer over the absorber temperature range studied
  - Initial enzyme loading for process established

UK-CAER Wetted Wall Column Schematic



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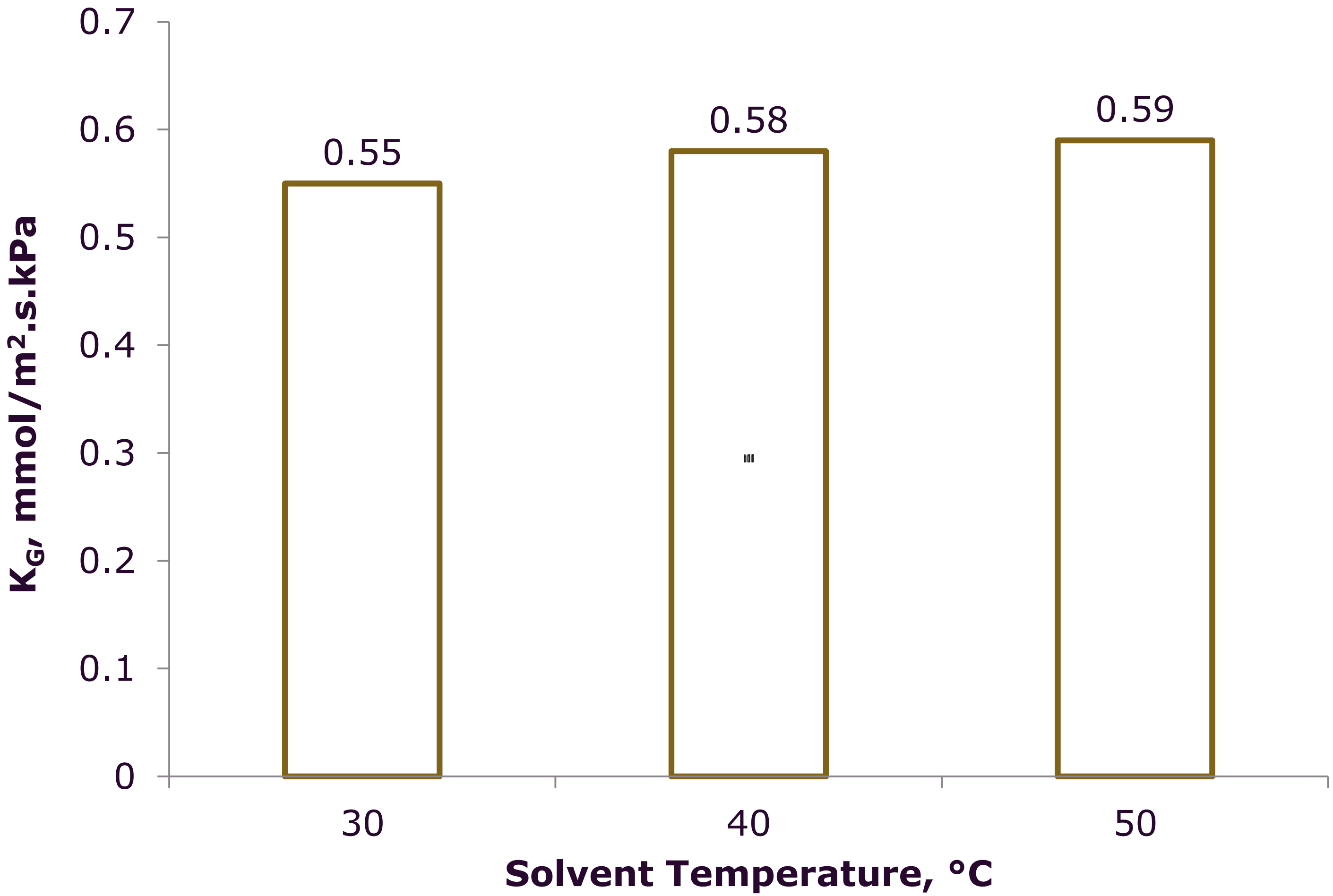
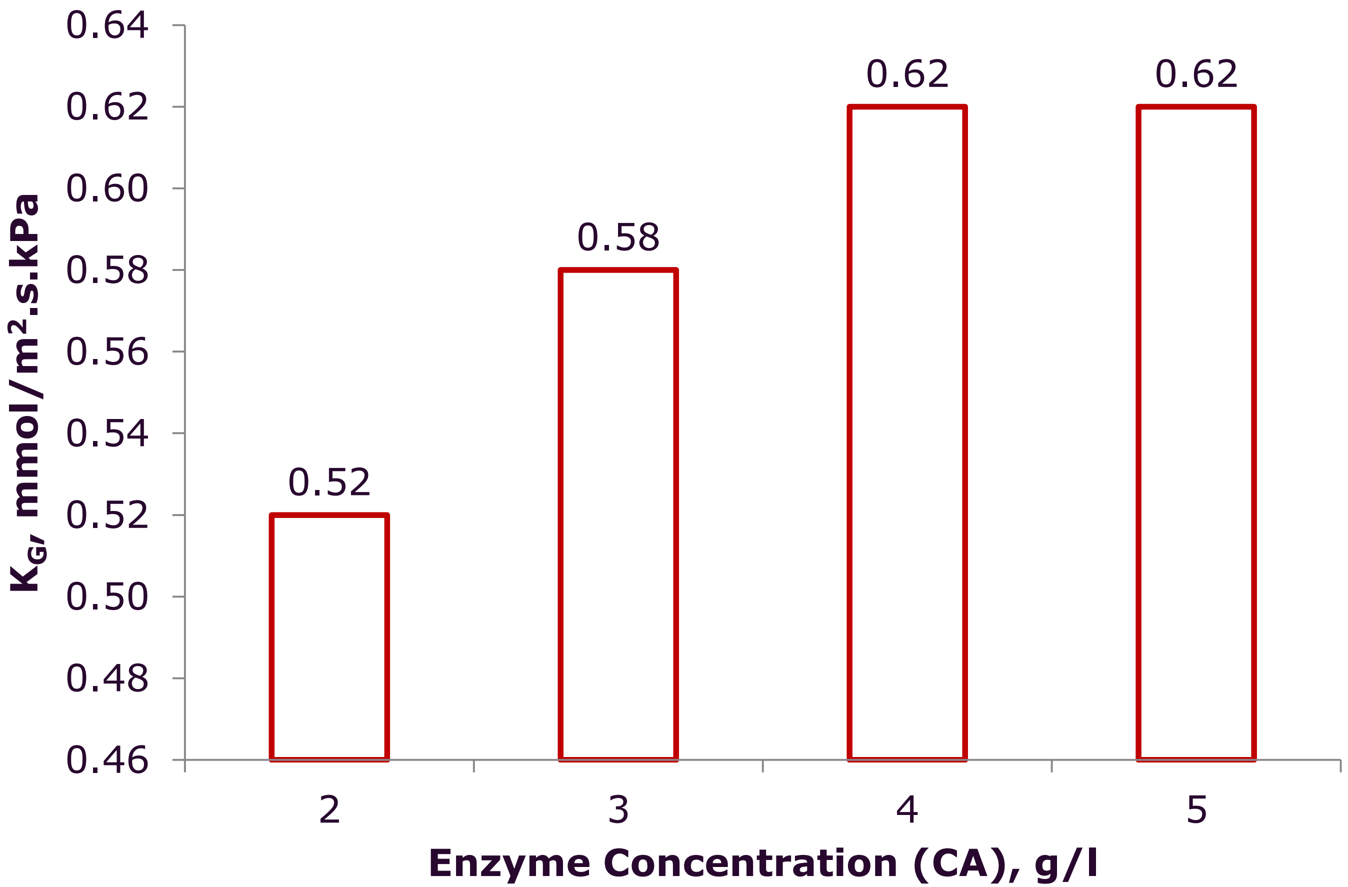
Measures gas to liquid flux

UK-CAER Mass Transfer Results



- Solvent: aq. 20% K_2CO_3 + carbonic anhydrase
- Temperature had minimal impact on mass transfer over the absorber temperature range studied

UK-CAER Mass Transfer Results



- Solvent: aq. 20% K_2CO_3 + carbonic anhydrase
- Achieved Initial Milestone Enzyme-catalyzed Solvent Kinetics (Mass Transfer)

Laboratory Validations - Summary

- Ultrasonic Unit Batch Testing
  - Demonstrated CO_2 release via ultrasonic energy addition
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  - Lab results show robustness to simulated process pH, ultrasonics, and absorber temp. with (manageable) losses at increased temp
- Absorption Kinetics
  - Temperature had minimal impact on mass transfer over the absorber temperature range studied
  - Initial enzyme loading for process established

> Lab results were provided for prefeasibility study

Preliminary Technical and Economic Feasibility

- Overall CO_2 Capture Reaction

$$CO_2 + H_2O + K_2CO_3 \underset{\text{CA Enzyme}}{\leftrightarrow} 2KHCO_3$$

- Aspen Plus® (with Radfrac) used for Process modeling for absorption
- AspenTech's Capital Cost Estimator® along with budget supplier quotations used for Cost Estimation of the PCC Components
- Preliminary techno-economic feasibility and sensitivity studies performed based on the fixed coal feed rate as per Case 10 (MEA-based) for the enzyme enhanced K_2CO_3 solvent.
- Four methodologies of regeneration have been investigated:

  Case 1: Vacuum Stripping using LP steam

  Case 2: Vacuum Stripping using VLP steam

  Case 3: Ultrasonic regeneration using electrical energy

  Case 4: Ultrasonic regeneration using VLP steam novozymes Rethink Tomorrow

Conclusions and Recommendations

- Preliminary techno-economic evaluation has been completed for the process integrated with a subcritical coal-fired power plant indicating net efficiency improvement of 25% versus Case 10.
- Net Plant Efficiency (on HHV basis) and LCOE ($/MWh$_e$):

		Net efficiency	LCOE ($/MWh$_e$)
	Case 10	24.9%	119.6
Power Equivalent of 0.0911 Kwh/lb of steam	Vacuum Regeneration	24.34% – 29.97%	112.92 – 125.23
	Ultrasonic Regeneration	26.63% – 31.41%	108.90 – 117.50
Power Equivalent of 0.0665 Kwh/lb of steam	Vacuum Regeneration	24.07% - 27.75%	117.56 – 126.06
	Ultrasonic Regeneration	24.41% - 29.19%	113.02 – 123.29

- Challenges that will be investigated in the next phases of the project are:
  - Validation and optimization of the performance, design of the ultrasonic regeneration
  - Reduction in dosing quantity of the enzyme
  - Further investigation of the option to utilize a VLP for solvent regeneration
  - Utilization of alternative materials of construction to reduce the capital cost of plant

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Project Schedule – Next Steps

- Task 1 – Project Management and Planning
- Task 2 – Process optimization
  - Ultrasonic Unit Optimization
  - Solvent & Enzyme-Solvent Compatibility Optimization
  - Solvent Physical Properties & Kinetic Measurements
  - Design Integrated Bench-Scale System
- Task 3 – Initial Technical & Economic Feasibility

- Task 4 – Bench Unit Procurement & Fabrication
- Task 5 – Unit Operations Shakedown Testing & Integration
- Task 6 – Bench-scale Testing
- Task 7 – Full Technology Assessment

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